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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 11].

THREE ADDITIONS TO THE KOHLRAUSCH-OSTWALD CONDUCTIVITY METHOD.

BY J. LIVINGSTON R. MORGAN.

Received November 2, 1899.

THE Kohlrausch-Ostwald method for determining the electrical conductivity of electrolytes by means of an alternating current and telephone is very accurate and easy to use so long as the induction coil gives a clear high note. This condition, however, is not easy to fulfil, for, owing to the magnetization of the steel spring current breaker, the adjustment is soon lost. This objection holds for all coils which use steel for the vibrator whether in the form of a spring or wire. In preparing four sets of apparatus for conductivity so much difficulty was experienced in adjusting the coils that it was decided to find, if possible, another form of interruptor which would be free from this objection. As a result of this search an attachment was found which not only gives a clear high note, and allows of rapid adjustment, but which can be used for one set or for a number of sets of apparatus so that in the latter case all may be adjusted by one operation. Each piece of apparatus is

set up as usual except that the current breaker is removed from each coil, the interrupting being done for all in another room by an apparatus run by another source of electricity. This apparatus is a modified form of Professor M. I. Pupin's electrodynamic interruptor. The modifications referred to consist in the use of an electromagnet instead of the somewhat uncommon Weston permanent one, and in the interruption of a separate circuit instead of that which causes the string to vibrate. A

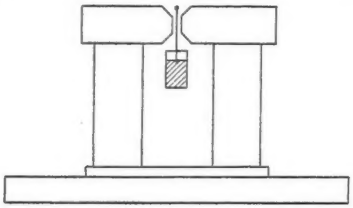

Fig. 1.

horseshoe electromagnet with special pole pieces (Fig. 1) is mounted vertically upon a base-board. On these pole pieces is fastened an oblong framework of brass, on the ends of which are screw devices to which the ends of a brass wire may be soldered and kept at any desired tension, between the pole pieces. Two mercury cups are placed the one in front and the other behind the magnet into each of which dips a short piece of amalgamated

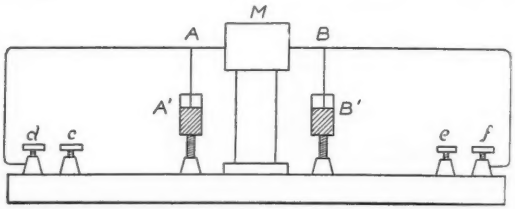

Fig. 2.—*c* is connected to B' and *e* to A' underneath the base. The current enters at *d* and *c* and one portion goes to the electromagnet M by wires not shown in the figure.

copper wire which is soldered to the brass wire. These mercury cups are so arranged upon screws that they may be raised or lowered so as to be in contact with the copper dippers. Fig. 2 shows the arrangement of the wire, cups and magnet with their connections. The current (three to six volts, taken from the

[1] *Am. J. Sci.*, 3d series, 45, p. 325 (1893).

electric light circuit or from storage cells) enters at the two binding-posts *c* and *d* and divides one portion going to the magnet through wires not shown in the figure, the other going from *c* through the wire to B, to the mercury at B′ and back to *d*. When the current is flowing in this way, the wire is repelled by the magnet so that the contact at B′ is broken but made again instantaneously by the tension of the wire. In this way the wire is retained in rapid vibration, and, if the cup A is properly adjusted, any battery circuit connected through *e*, A′, A, and *f* will be interrupted. By connecting a Leclanché cell with an induction coil (with the breaker removed) through the two binding-posts *e* and *f* a rapidly alternating current is obtained and a clear high adjustable

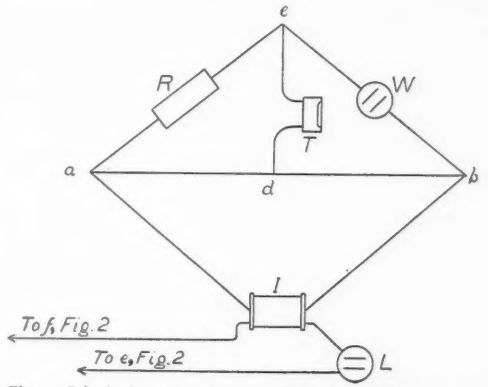

Fig. 3.—R is the known resistance, W the electrolytic cell, I the coil, L the Leclanché cell and T the telephone.

note produced in the telephone. Fig. 3 shows the connections for a piece of apparatus set up in the way described so that no further explanation is necessary. Naturally any number of sets may be connected in this way through the interruptor, the same tone being obtained in all, and all may be adjusted at once. If the current necessary for the operation of the vibrator were not so great only one mercury cup would be necessary, but it has been found more satisfactory to simply interrupt the current from a single cell and thus to avoid heating and polarization effects at the electrodes. The arrangement described has been in use in

this laboratory for more than a year and has given great satisfaction.[1]

The second addition is designed for use in determining the conductivity of water or other substances of high resistance. In such cases in using the simple Ostwald form of bridge, the reading is very near one end so that the possible error, due to bad end contact, is very large. The arrangement proposed lengthens the bridge, only the one small portion represented by the one meter of wire being used, and so all readings are multiplied by a certain factor, and caused to approach the middle of the wire where the results are most accurate. This end is reached by placing certain lengths of insulated bridge wire on spools between the actual bridge wire and the arm of the bridge (between *b* and *W* Fig. 3). Spools containing four, nine, and nineteen meters of the bridge are prepared so that by inserting these, with mercury contacts, the readings are multiplied by five, ten, and twenty, respectively, that spool being used which brings the reading nearest the middle of the bridge. The idea is employed in the more elaborate bridges used by physicists, and also in the simple Ostwald form for the determination of electromotive force[2] but, so far as I know, it has never been used for conductivity. Its results, however, are very satisfactory and the idea is recommended to others.

The third addition proposed is for the purpose of ascertaining, as quickly and accurately as possible, that point on the bridge which gives the minimum tone in the telephone. The regular method of determining this point is first to locate it approximately and then to fix it by finding two points, one on either side of it, at which the tone has the same intensity. When these two points have been found the reading midway between them gives the minimum. In using this method it is hard to match the two tones since it takes an appreciable time to move the sliding contact. If the two tones could follow one another immediately it would be very much simpler. To do this the block of wood which is used as the holder for the sliding contact is provided with two press keys instead of one, both being connected by the same binding-post. The contact points of these two press keys should be

[1] Messrs. Eimer & Amend of New York City are prepared to make interruptors of this kind to order at a cost of ten dollars each.

[2] Goodwin: *Ztschr. phys. Chem.*, 13, 290 (1894).

either one-half or one centimeter apart and have vulcanite knobs upon which to rest the fingers. As soon as the approximate reading is found with one key the block is moved until both keys when pressed give a tone of the same intensity; the middle point is then the true minimum. It is well to have the one key movable so that the distance between the contacts may be reduced as the point is reached. By the use of this arrangement it is possible to find the point within a small fraction of a millimeter and much less experience is necessary for accurate results than by the ordinary process.

ON THE SURFACE-TENSIONS OF MIXTURES OF SULPHURIC ACID AND WATER, AND THE MOLECULAR MASS OF SULPHURIC ACID.

By C. E. Linebarger.

Received October 25, 1899.

THE apparatus employed in making the measurements of the surface-tension was that described in a previous number of this Journal.[1]

The sulphuric acid used was Baker and Adamson's "chemically pure" (sp. gr. 1.84), and was found on analysis to contain 4.98 per cent. of water. This acid was mixed in varying proportions with water and the mixtures analyzed. The specific gravities of some of the mixtures were determined, but most of them were taken from Lunge and Isler's tables[2] and the corrections for temperature applied by means of the data given by Bineau.[3]

The thermostat consisted of a beaker filled with water and provided with a stirrer. A layer of heavy oil was poured over the water so as to prevent evaporation. Readings were taken (never less than three at the same temperature) at intervals of about 5°. These were plotted and a smoothed curve (which was approximately a straight line) drawn through them. From this curve, readings were taken at temperature-intervals of 10°, and these were used in calculating the surface-tensions.

Readings were taken in the same way with pure water, from which with the aid of Ramsay and Shields' data[4] on the surface-

[1] This Journal, **18**, 514 (1896).
[2] *Ztschr. angew. Chem.*, 129 (1890). Landolt and Börnstein, 196.
[3] *Ann. chim. phys.* (3), **26**, 123 (1849).
[4] *Ztschr. phys. Chem.*, **12**, 433 (1893).

tension of water at various temperatures, the values of the "apparatus constant" were calculated for every 10°. These were found to change slightly but regularly.

The numerical results of the determinations are given in the following table and are represented graphically in Figs. I and II. Curves for 0°, 20° and 50° only are drawn in Fig. I so as not to crowd too much. As it is, the right-hand parts of the curves practically coincide.

SURFACE-TENSIONS OF MIXTURES OF SULPHURIC ACID AND WATER.

Temperature.	Apparatus constant.	Distance between ends of tubes in 0.025 inch.	Specific gravity.	Surface tension in dynes per cm.
		2.65 per cent. H_2SO_4.		
0°	1.260	56.39	1.021	73.60
10°	1.266	55.71	1.019	72.69
20°	1.273	54.83	1.017	72.02
30°	1.278	54.04	1.015	71.13
40°	1.283	53.12	1.013	70.07
50°	1.290	52.13	1.011	69.01
		5.16 per cent. H_2SO_4.		
0°	1.260	55.83	1.037	74.02
10°	1.266	55.01	1.035	73.14
20°	1.273	54.18	1.033	72.31
30°	1.278	53.31	1.031	71.29
40°	1.283	52.43	1.029	70.43
50°	1.290	51.54	1.027	69.33
		11.87 per cent. H_2SO_4		
0°	1.260	54.02	1.081	74.75
10°	1.266	53.46	1.078	74.10
20°	1.273	52.86	1.075	73.48
30°	1.278	52.15	1.072	72.58
40°	1.283	51.32	1.069	71.52
50°	1.290	50.41	1.066	70.45
		18.33 per cent. H_2SO_4.		
0°	1.260	51.61	1.138	75.30
10°	1.266	51.00	1.133	74.44
20°	1.273	50.37	1.128	73.59
30°	1.278	49.72	1.125	72.75
40°	1.283	49.05	1.123	71.92
50°	1.290	48.30	1.118	70.90
60°	1.296	47.64	1.113	69.95
70°	1.303	46.87	1.108	68.89

35.13 per cent. H_2SO_4.

Temperature.	Apparatus constant.	Distance between ends of tubes in 0.025 inch.	Specific gravity.	Surface tension in dynes per cm.
0°	1.260	47.03	1.275	77.19
10°	1.266	46.75	1.268	76.68
20°	1.273	46.41	1.262	76.34
30°	1.278	46.05	1.255	75.45
40°	1.283	45.67	1.248	74.68
50°	1.290	45.26	1.242	74.05
60°	1.296	44.76	1.235	73.15
70°	1.303	44.22	1.228	72.25

58.05 per cent. H_2SO_4.

0°	1.260	40.03	1.494	77.60
10°	1.266	39.98	1.486	77.44
20°	1.273	39.95	1.478	77.25
30°	1.278	39.88	1.470	77.08
40°	1.283	39.78	1.462	76.76
50°	1.290	39.66	1.454	76.49
60°	1.296	39.46	1.446	76.03
70°	1.303	39.22	1.438	75.55

65.27 per cent. H_2SO_4.

0°	1.260	37.75	1.575	77.41
10°	1.266	37.74	1.567	77.34
20°	1.723	37.72	1.559	77.29
30°	1.278	37.70	1.531	77.13
40°	1.283	37.68	1.543	76.99
50°	1.290	37.65	1.535	76.89
60°	1.296	37.61	1.527	76.74
70°	1.303	37.40	1.519	76.31

80.45 per cent. H_2SO_4.

0°	1.260	28.84	1.752	66.60
10°	1.266	28.78	1.743	66.40
20°	1.273	28.65	1.734	66.32
30°	1.278	28.60	1.725	66.00
40°	1.283	28.56	1.716	65.92
50°	1.290	28.55	1.707	65.79
60°	1.296	28.50	1.698	65.67
70°	1.303	28.48	1.689	65.50

83.23 per cent. H_2SO_4.

0°	1.260	27.11	1.783	64.18
10°	1.266	27.09	1.774	64.09
20°	1.273	27.06	1.764	63.89

Temperature.	Apparatus constant.	Distance between ends of tubes in 0.025 inch.	Specific Gravity.	Surface tension in dynes per cm.
30°	1.278	27.02	1.755	63.70
40°	1.283	27.00	1.746	63.54
50°	1.290	26.99	1.737	63.48
60°	1.296	26.97	1.728	63.37
70°	1.303	26.96	1.718	63.19
		95.02 per cent. H_2SO_4.		
0°	1.260	23.63	1.843	58.26
10°	1.266	23.54	1.833	57.97
20°	1.273	23.46	1.824	57.76
30°	1.278	23.40	1.814	57.53
40°	1.283	23.39	1.805	57.43
50°	1.290	23.36	1.796	57.36
60°	1.296	23.31	1.786	57.28
70°	1.303	23.24	1.775	56.89

The foregoing data show that both the addition of water to sulphuric acid and of sulphuric acid to water increases the surface-tension of the liquids. The increase in the surface-tension of the acid even when but a small proportion of water is mixed with it is especially marked. The maximum surface-tension is observed when about equal quantities of the two liquids are mixed. It is also shown that certain mixtures of sulphuric acid and water, although of different percentage composition, may yet have equal surface-tensions. This is clearly brought out in the curves for mixtures containing 58.05 per cent. and 65.27 per cent., respectively, of the acid; the curves cross at an abscissa-value of about 22°. Besides this observed instance, other mixtures have a similar behavior. The limits of the values of their composition and surface-tensions may be learned by an inspection of the figures.

A noteworthy peculiarity of strong solutions of sulphuric acid in water is the slight influence that changes of temperature have upon their surface-tensions. The curves in Fig. 2 become more and more horizontal the greater the percentage of acid in the mixtures. From these low values found for the temperature coefficients, certain conclusions may be drawn as to the degree of molecular polymerization of pure sulphuric acid. It is true that no determinations were made of the surface-tension of the pure acid, but it seems reasonable to conclude that the regularity of

the curves would extend to the abcissa-value of the pure acid. Yet it is scarcely to be expected that anything like correct values for the surface-tension of the pure acid would be obtained by

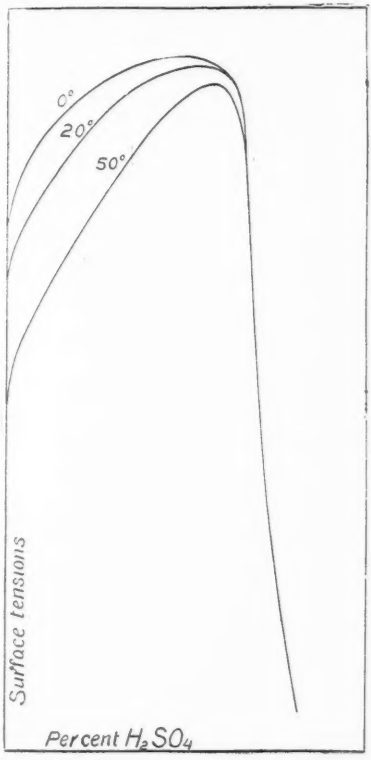

Fig. 1.

extrapolation, for the curves are too steep and close together. All that is legitimate to infer is that the pure acid has a small temperature coefficient with respect to its surface-tension.

Now according to the views of Ramsay and Shields[1] the degree of polymerization of a liquid may be estimated by means of the change of its molecular surface energy with the temperature. The smaller this is, the greater is the degree of polymeri-

[1] *Loc. cit.*

zation of a liquid's molecules. The small temperature coefficient of sulphuric acid points then to a high degree of polymerization; the molecular mass of its molecule must be several times 98, the molecular mass corresponding to the formula H_2SO_4. Ramsay

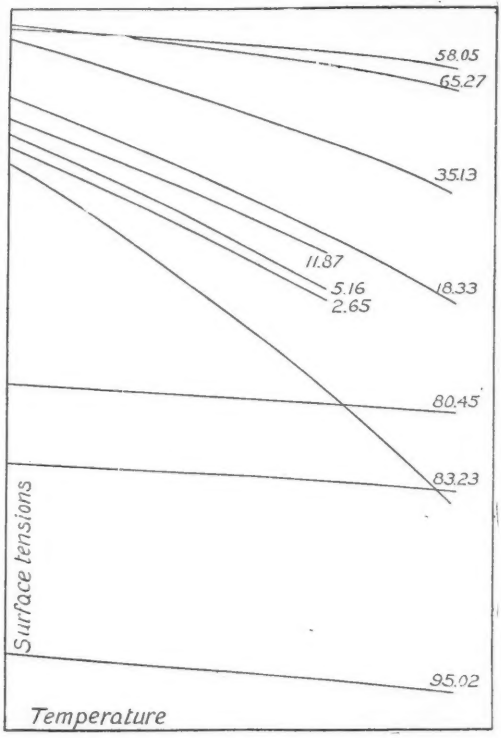

Fig. 2.

in a lecture before the Chemical Society of Paris[1] stated that he had found it probable that the molecule of sulphuric acid could be approximately represented by the formula $(H_2SO_4)_{23}$. If this be true, sulphuric acid has the most complex molecule of any liquid as yet examined in that regard, and this complexity of

[1] This was printed in the *Revue Scientifique* (4), **2**, 1 (1894). No data or details seem to have been given in any of the journals devoted to the publication of chemical research.

molecular structure may account for many of the anomalous properties of mixtures of sulphuric acid and water.

The conclusion that sulphuric acid is molecularly polymerized to a very considerable extent would indicate in accordance with the views of Nernst[1] and Brühl[2] that the pure acid should have a large dielectric constant and high dissociative power. The specific inductive capacity of sulphuric acid has not been determined and no measurements of the electric conductivity of salts dissolved in it have been made. The electric conductivity of a concentrated acid may, indeed, be regarded as due to the ions of water, for the acid may be considered to be the solvent and water the dissolved substance. If the dielectric constant of pure sulphuric acid should be found to be larger than that of water, it seems in the light of the views of Nernst and Brühl quite natural to suppose that the acid would exert a not inconsiderable dissociative power on water. Still even in concentrated acid, the extraordinary dissociative power of water would assert itself, and the acid regarded as solvent would become dissociated into its ions in part. The circumstance that the acid may dissociate into more than two ions together with the probability that it is molecularly polymerized, complicates matters greatly.

The fact found by Kohlrausch[3] that a 10 per cent. solution of water in sulphuric acid presents a maximum of conductivity may perhaps be taken as an indication that the acid actually does assert a dissociative action on water; that the conductivity of stronger solutions of acid in water are quite small may be due to the great viscosity of the acid solvent. It would be premature, however, to enter more at length into discussions of this nature, because of the fewness of the data and because the work of Kahlenberg and Lincoln[4] shows that not so very much reliance can be placed on the views of Nernst and Brühl.

[1] *Ztschr. phys. Chem.*, **13**, 3 (1894).
[2] *Ibid.*, **18**, 514 (1895) and **27**, 317 (1898).
[3] Pogg. *Ann.*, **159**, 233 (1876).
[4] *J. Phys. Chem.*, **3**, 12 and 457 (1899).

ON HUBL'S IODINE METHOD FOR OIL ANALYSIS.

By Augustus H. Gill and Walter O. Adams.

Received November 29, 1899.

THIS method, as is well known, depends upon the fact that the unsaturated glycerides in the oils form addition products with iodine: it has the disadvantage that substitution products—the amount varying with the time of action and strength of the solution—are formed as well. If their formation could be prevented the test would be much increased in value and it was to ascertain if this were possible that this investigation was undertaken.

As ordinarily prepared, the solution contains mercuric chloride and iodine in alcohol: by their interaction mercuric chloriodide and iodine chloride are formed[1] and it is supposed that the latter is the active agent.

$HgCl_2 + I_2 = HgClI + ICl$. Ephraim[1] and also Wijs[2] have shown that practically the usual iodine numbers are obtained when a solution of iodine chloride in alcohol is employed. Schweitzer and Lungwitz[3] found that mercuric bromide caused a larger iodine number than the chloride: "that manganese bromide, cadmium, nickel and cobalt chlorides cause practically no addition[4] and that the latter gives the highest true iodine addition figure." As with mercuric chloride, there is no reason why mercuric bromide might not similarly form iodine bromide and this be the active agent.

These metallic salts may play another part in the reaction besides the formation of iodine chloride, that of carriers of halogen, similiar to that played by mercury in the Kjeldahl process when dissolving the substance in sulphuric acid. That some such agent is necessary, is shown by the results of Gantter,[5] who found that a solution of iodine in carbon tetrachloride acts very slowly upon the oil and that the results are irregular,— a result which the authors can substantiate, both with oils and oleic acid.

The substance selected as a carrier in the following experiments

1 *Ztschr. angew. Chem.*, 284 (1895).

2 *Ber. d. chem. Ges.*, **31**, 750.

3 *J. Soc. Chem. Ind.*, **14**, 1031.

4 It would seem as if this should be "substitution."—Author.

5 *Ztschr. anal. Chem.*, **32**, 181.

was mercuric iodide, and as it is more soluble in methyl than ethyl alcohol the former was employed: that used was free from acetone and anhydrous, being distilled from quicklime. Thirty grams of mercuric iodide and 25 grams of sublimed iodine were dissolved in a liter of methyl alcohol; of this solution 30 cc. were employed for each test and the customary procedure followed. Oleic acid and various oils were used to test the efficacy of this solution; the oleic acid was the purest obtainable, and gave no test for stearic acid.

The results are given in the accompanying table:

AMOUNT OF IODINE ABSORBED BY VARIOUS ACIDS AND OILS.

A. Acids.

Substance.	Time. Hrs.	Hübl.		Iodide.
Stearic Acid.	4	8.99		7.25
		8.70		6.97
		8.82		6.93
Average.		8.84		7.05
Oleic Acid.	4	101.0	91.31	89.19
		100.9	89.64	89.39
		103.5	90.93	90.54
Average.		101.7	90.2	
	3	—-	89.10	89.23
	20	99.38[1]		97.88[1]
		98.41		97.50
		98.37		97.65
	25	——		98.02
				97.70
				97.88

B. Oils.

Substance.	Time. Hrs.	Hübl.	Iodide.		
Olive.	4	82	78.9	79.0	79.3
Cottonseed.	4	107	91.6	91.2	92.9
Prime lard.	4	74	72.4	71.6	71.5
Neatsfoot.	4	59	55.8	56.0	55.6

It will be noticed in the case of stearic acid, which should have no iodine absorption, that the substitution, while not

[1] As is evident, considerable substitution has taken place here: this when corrected for gave the theoretical value, 90. This is at variance with the observation of Schweitzer and Lungwitz, *loc. cit.*, 1034.

entirely avoided, is materially lessened by about 20 per cent. With oleic acid, the numbers obtained by the iodide process average but 0.2 per cent. higher than the theoretical, 90 per cent., which is the closest agreement, so far as known, obtained by any process; they are 11 points lower than those obtained by the usual Hübl process. A slight substitution did occur as shown by the hydriodic acid liberated. This was increased by lengthening the time of action of the solution, as seen from the 20- and 25-hour tests; the 3-hour test was conducted to determine if the substitution could not be eliminated by a shorter time. It was found that it did take place, indicating apparently that substitution and addition occur simultaneously: a small amount of substitution was found in the case of the oils as well as with oleic acid.

Attention was called in the early part of this paper to the fact that alcoholic solutions of iodine caused a low and variable addition of halogen to oleic acid; this is more particularly the case if carbon tetrachloride be used as a solvent; chloroform seems to increase this addition very materially. With the former, 66.74, 67.32, and 65.46 per cent. of iodine were added to oleic acid, whereas with the latter, 89.02, 83.66, and 85.86 per cent. were added.

As the solution used contained no halogen but iodine, thus excluding the formation of halides of iodine, and no water, excluding the liberation of oxygen, it would seem that we had here a method which, while as ready of application as the original Hübl, possessed the additional advantage of giving the true iodine figure.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, November, 1899.

THE IODOMETRIC DETERMINATION OF SMALL QUANTITIES OF CARBON MONOXIDE.

BY LEONARD P. KINNICUT AND GEORGE R. SANFORD.

Received November 2, 1899.

IN a previous paper[1] one of us mentioned that there might be more danger to be apprehended from the continuous breathing of air containing very small amounts of water gas, such as

[1] *Municipal Engineer*, 17, 71.

might occur from imperfection in gas fittings than from sewer gas or arsenical wall papers. It is known that air containing 0.3 per cent. of carbon monoxide causes death, 0.2 per cent. very dangerous symptoms, and that mice quickly show the effect of the gas when the air contains only 0.05 per cent. There is reason to believe that air containing even much smaller quantities when breathed for a number of hours may have an effect on the human organism, and on this account the detection and quantitative determination of very small amounts of carbon monoxide when mixed with large volumes of air is a question of importance.

The methods of detecting and estimating very small amounts of carbon monoxide may be divided into two classes: first, those in which carbon monoxyhemoglobin is formed; second, those in which it is oxidized to carbon dioxide. Those of the first class are of little value except for the detection of the gas and they may all be considered as modifications of Hoppe-Seyler's method, first published in 1864,[1] which is based on the fact that while both carbon monoxyhemoglobin, formed by the action of carbon monoxide on arterial blood, and oxyhemoglobin, give two absorption bands in the spectrum; oxyhemoglobin is alone reduced to hemoglobin by the action of such reducing agents as ferrous sulphate or ammonium sulphide.

The method of determining carbon monoxide by oxidation to carbon dioxide has not, until the past few years, received much attention. This oxidation can be accomplished by the use of many oxidizing agents, but of all of those which have been proposed iodine pentoxide is, from our experience, the one that can best be used for the determination of small amounts of carbon monoxide.

Ditte,[2] in 1870, showed that at temperatures between 150°–200° iodine pentoxide was decomposed by carbon monoxide, iodine and carbon dioxide being formed.

$$I_2O_5 + 5CO = I_2 + 5CO_2.$$

This reaction was seemingly first used by C. de la Harpe and F. Reverdine[3] for the detection of the gas, and Nicloux[4] and

[1] *Ztschr. anal. Chem.*, **3**, 439 (1864).
[2] *Bull. Soc. Chim.*, **13**, 318 (1870).
[3] *Chem. Ztg.*, **12**, 1726 (1888).
[4] *Compt. rend.*, **126**, 746.

Gautier[1] have made use of the reaction for its quantitative determination.

Nicloux determined the iodine set free, by the depth of color formed in a chloroform solution, and Gautier by the amount of carbon dioxide formed. We have not, by either of these methods, been able to obtain accurate determinations of small amounts of carbon monoxide, but have obtained most satisfactory results by determining the amount of iodine set free, with an N/1000 solution of sodium thiosulphate.

The apparatus used was, with slight changes, that described by Nicloux. Twenty-five grams of iodine pentoxide were placed in a small U-tube, which was suspended in an oil-bath and connected with a Wolff blood absorption tube containing 0.5 gram potassium iodide dissolved in 5 cc. water. The tube containing the iodine pentoxide was also connected with two U-tubes, one containing sulphuric acid, the other small pieces of potassium hydroxide, so as to remove from the air to be analyzed before it came in contact with the iodine pentoxide all unsaturated hydrocarbons, hydrogen sulphide, sulphur dioxide, and similar reducing gases. In all the experiments the oil-bath in which the U-tube containing the iodine pentoxide was suspended, was heated to 150° C., as preliminary tests showed that the reaction was not a quantitative one at lower temperatures.

The iodine pentoxide was made by the action of nitric acid on resublimed iodine, and after this substance had been purified by the usual methods the last traces of free iodine were removed by passing air, freed from all reducing substances, through the iodine pentoxide contained in a U-tube heated to 150° C.

In the experiments which were made to determine the accuracy of the above process, 1 liter of air was usually taken, but as seen in the following tables amounts as small as 250 cc. were tried in several cases and the rate at which the air was passed through the tubes was about 1 liter in two hours, the rate being controlled by forcing the air out of the bottle in which it was contained by dry redistilled mercury, the flow of which was regulated by a glass stop-cock. The amount of carbon monoxide added to the air was accurately measured from a tube made of capillary glass tubing and accurately calibrated so that each

[1] *Compt. rend.*, 126, 931.

division represented 0.005 cc., and readings of 0.001 cc. could easily be made. The temperature and barometric pressure were carefully noted and all volumes were reduced to 0° C. and 760 mm. pressure, and the determination of the iodine set free was made in the Wolff blood absorption apparatus which contained the potassium iodide solution.

With this apparatus, used as described, we were able to determine as small an amount as 0.025 cc. of carbon monoxide, when contained in 1000 cc. of air, or 0.0025 per cent. by volume. The following table gives the results obtained:

ANALYTICAL RESULTS.

Volumes taken.		Iodine liberated.		
Air.	Carbon monoxide.	Theoretical.	Found.	Difference.
cc.	cc.	Mg.	Mg.	Mg.
1000	0.410	0.941	0.907	0.034
1000	0.286	0.6575	0.6375	0.020
1000	0.359	0.8178	0.7832	0.0346
1000	0.170	0.3859	0.4540	0.0081
1000	0.211	0.4809	0.4775	0.0034
1000	0.151	0.3442	0.3252	0.019
1000	0.115	0.2639	0.2758	0.012
1000	0.061	0.1391	0.1431	0.004
1000	0.023	0.0535	0.0494	0.0041
1000	0.029	0.0672	0.0689	0.0017
1000	0.023	0.0535	0.0495	0.004
500	0.131	0.2993	0.2976	0.0017
250	0.030	0.06862	0.07165	0.0029
250	0.026	0.05967	0.05855	0.0011

Volumes taken.		Carbon monoxide.		
Air.	Carbon monoxide	Calculated. Per cent. By volume.	Found. Per cent. By volume.	Difference.
cc.	cc.			
1000	0.410	0.041	0.0395	0.0015—
1000	0.286	0.0286	0.0278	0.0008—
1000	0.359	0.0359	0.0341	0.0018—
1000	0.170	0.0170	0.0197	0.0027+
1000	0.211	0.0211	0.0208	0.0003—
1000	0.151	0.0151	0.0142	0.0009—
1000	0.115	0.0115	0.0119	0.0004+
1000	0.061	0.0061	0.0062	0.0001+
1000	0.023	0.0023	0.0021	0.0002—
1000	0.029	0.0029	0.0030	0.0001+
1000	0.023	0.0023	0.0022	0.0001—
500	0.131	0.0262	0.0260	0.0002—
250	0.030	0.0120	0.0124	0.0004+
250	0.026	0.0104	0.0100	0.0004—

These results showed that by the above method accurate determinations could be made of very small amounts of carbon monoxide in pure air, and it only remained to be proved that the accuracy of the process was not affected when the carbon monoxide was mixed with air containing illuminating gas, and experiments were made to determine the action of hydrogen, marsh-gas, unsaturated hydrocarbons, hydrogen sulphide, and sulphur dioxide on iodine pentoxide.

Hydrogen and marsh-gas, as was to be expected, had no effect on the iodine oxide at 150°C. and the unsaturated hydrocarbons, hydrogen sulphide and sulphur dioxide, in much larger amounts than are contained in illuminating gas, or formed by its combustion, were perfectly absorbed, when passed in the way described through U-tubes containing sulphuric acid and potassium hydroxide.

These facts having been determined, mixtures of illuminating gas and air were made, and the amount of carbon monoxide determined.

The experiments gave the following results:

The gas used contained 18.6 and 19.0 per cent. of carbon monoxide, respectively. Of the first, 0.104 cc. was added to 1 liter of air and the air was found to contain 0.019 cc. carbon monoxide, the calculated amount being 0.0191 cc. In the second case, 0.146 cc. of the gas was taken and the air gas found to contain 0.027 cc. of carbon monoxide in place of 0.02789 cc.

The results that have thus been obtained show that the presence and amount of carbon monoxide in the air of a room can be determined when the air contains above 0.0025 per cent. by volume, or 2.5 volumes in 100,000 volumes of air, and if the presence of this gas is due to leakage of illuminating gas and the per cent. of carbon monoxide in this gas is known, the amount of illuminating gas contained in the air can, of course, approximately be calculated.

WORCESTER POLYTECHNIC INSTITUTE.
November, 1899.

THE TECHNICAL ANALYSIS OF LICORICE PASTES.

By M. Trubek.

Received November 14, 1899.

WHEN I was first confronted with the analysis of licorice products, I had to select a method, which, giving the necessary data required by the trade, could easily be carried out in a reasonably short time.

The literature on that subject was found to be rather meager and only fragments could be found here and there. More comprehensive was the article on the subject of licorice found in Hager's *Pharmaceutische Praxis*, and for the determination of some constituents the method therein described was at first carried out with a few minor modifications; instead of taking 10 grams of substance as prescribed only 2 grams were used. The first amount required too large quantities of ammonia and alcohol on one hand and absolute alcohol on the other hand to get a colorless filtrate, besides requiring too much time, extra large filters and weighing-bottles. It soon developed, however, that the above method gave too high results in glycyrrhizin, which results were out of question, in case glucose had been added to the paste, as the following figures will show:

	Glycyrrhizin. Per cent.
1. Paste with no glucose added	22.25
2. Same paste with 15 per cent. glucose added	29.61
3. " " " 20 " " " "	34.12

Instead of going down on glycyrrhizin as it should be through the addition of the glucose, the values for that substance rose with the amount of glucose added. It was examined for that substance as glucose might have been thrown down together with the glycyrrhizin and was not entirely removed during washing, by precipitating the glycyrrhizin with basic lead acetate but only about 2 per cent. of glucose were found in No. 2, not explaining the rise in glycyrrhizin. I concluded therefore that that rise was due to the presence of a substance or substances formed from the glucose by the ammonia, especially while concentrating the run-off from the first operation, which substances were absolutely insoluble in absolute alcohol and could not be washed out by the same. After several experiments along those lines the following mode of operation was adopted and found to work satisfactorily.

To 2 grams of the extract to be examined add 5 cc. water, place on a warm plate, and by means of a glass rod make up to a perfectly even mass. Add little by little, while stirring, 20 cc. of 96 per cent. alcohol and allow to settle. Filter through a weighed filter and wash with a mixture of 1 part water and 4 parts alcohol of above strength until run-off is colorless, which takes about 100 cc. of wash liquor. Keep the top of the filter wet, as it easily dries out and is then washed with difficulty. The filter, with contents, is dried at 105° C. for three hours and weighed. It gives the gummy matter, starch, etc., contained in the extract. The filtrate is either distilled off or evaporated. Take a large beaker for evaporating, or else liquor creeps up to the edges incurring losses. When nearly evaporated transfer to a small beaker, evaporate further to a thick sirup, making about 1 or 1.5 cc. It is then dissolved in 2 cc. glacial acetic acid, and 30 cc. absolute alcohol are added with constant stirring. Too violent stirring produces a lumpy mass, which is difficult to wash out. The solution is allowed to settle. Filter through a weighed filter, wash with absolute alcohol until no acid reaction, dry at 105° C. for three hours, and weigh. The figure obtained is not pure glycyrrhicic acid, but rather a salt. To get the acid sufficiently accurate, an aliquot part is incinerated, using blast heat at the end, and deducting 0.7 of the percentage of ash from the percentage of the salt found. The ash consists mainly of calcium oxide, but contains also very small amounts of alumina and magnesia.

The glycyrrhizin salt as prepared by my method represents a light yellow amorphous powder, soluble in glacial acetic acid, cold and hot water, and dilute alcohol. It has a very sweet taste. (The pure glycyrrhicic acid is according to Haberman[1] a tribasic acid and forms acid and normal salts. It dissolves in the same reagents as the salt above described, but only in hot water, while making a jelly with cold water.)

The filtrate from the glycyrrhizin is distilled off, diluted and evaporated, and this repeated until the acetic acid is driven off. The residue is dried at 105° C. for three hours and weighed. This amount represents the so-called extractive matters, containing the saccharine matter that the root contained originally or which had been added subsequently to the paste; they contain also some tannin, resin, etc.

1 *Ann. Chem.* (Liebig), 197, 105.

Ash, in the paste, is determined by incinerating 2 grams in a platinum dish. For total solids, about 5 grams are dissolved in hot water and made up to 500 cc. after cooling the liquor. It is well shaken and 50 cc. are evaporated, dried at 105° C. for three hours, and weighed.

For solids soluble in cold water, 50 cc. of the clear filtrate are evaporated, dried, and weighed. For evaporation, flat bottomed, so-called crystallizing glasses have been found to be very convenient.

The difference between "total solids" and "soluble solids" represents the residue insoluble in cold water.

The moisture is taken as the amount obtained by subtracting the "total solids" from 100.

Reducing substances are determined as usual after precipitating with basic lead acetate and titrating the filtrate, freed from lead, with standardized Fehling's solution.

Following are the results obtained by the above method from different samples of licorice extract:

	1. Per cent.	2. Per cent.	3. Per cent.	4. Per cent.
Moisture	24.18	25.14	19.58	23.99
Residue insoluble in cold water	3.95	6.79	14.35	2.54
" " " mixture of 1 water and 4 alcohol	27.27	25.20	36.58	24.65
Glycyrrhizin	22.78	21.97	18.51	19.90
Extractive matter	25.02	25.05	26.02	28.91
Ash	6.25	6.02	5.60	5.59
Reducing matters as glucose	....	....	....	9.76

Sample No. 1 was one of Scudder's brands.

Sample No. 4 gave, by the method described in Hager's *Pharmaceutische Praxis* for glycyrrhizin, 28.57 per cent..

An analysis of fresh and spent licorice root gave the following results:

	Fresh. Per cent.	Spent. Per cent.
Moisture	8.40	10.00
Total solids	33.18	10.86
Cold solubles	29.65	....
Gummy matter, starch, etc	8.07	3.56
Glycyrrhizin	11.21	2.25
Extractive matters	14.77	5.60
Ash	2.68	0.55
Reducing matters	0.52	....

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BENZENESTEAROSULPHONIC ACID AND OTHER SULPHONIC ACIDS CONTAINING THE STEARIC RADICAL.[1]

By E. Twitchell.

Received November 29, 1899.

IN connection with some experiments on the action of sulphuric acid on the higher fatty acids I prepared a mixture of benzene and oleic acid and treated this with an excess of concentrated sulphuric acid. I found that a union took place between the benzene and the oleic acid, and at the same time a sulphonic acid was formed.

$$C_6H_6 + C_{18}H_{34}O_2 + H_2SO_4 = C_6H_4(SO_3H)C_{18}H_{35}O_3 + H_2O.$$

To prepare this benzenestearosulphonic acid, a mixture of oleic acid and benzene is treated with a large excess of concentrated sulphuric acid, avoiding any excessive rise in temperature by cooling the mixture and by adding the acid slowly. After several hours the greater part of the oleic acid will have combined as expressed by the above equation, and the benzenestearosulphonic acid can be separated and freed from the excess of the original components of the mixture and from the results of secondary reactions which have occurred.

A consideration of the action of sulphuric acid on oleic acid will make it plain that these impurities can only be the following:

1. Unacted-on oleic acid;
2. Other fatty matters, such as oxystearic acid and fatty anhydrides, produced by the action of the sulphuric acid and subsequent decomposition of the sulpho compounds;
3. Unacted-on benzene;
4. Stearosulphuric acid, $C_{18}H_{35}O_2.HSO_4$;
5. Benzenesulphonic acid;
6. Sulphuric acid in large excess.

From its mixture with these substances the pure benzenestearosulphonic acid can be separated by virtue of the following properties it possesses, to which I will again refer: It is soluble

[1] Read before the meeting of the Cincinnati Section, November 15, 1899.

in water, but can be rendered completely insoluble (salted out) by the presence in the water of a little hydrochloric acid or sulphuric acid. It is very stable, not decomposed by boiling with acid solutions. It is insoluble in petroleum ether.

The reaction mixture is treated with water and heated to boiling, whereby the excess of sulphuric acid is diluted and the mass separates into two layers; the lower, a clear aqueous liquid, contains the excess of sulphuric acid and whatever benzenesulphonic acid may have been produced. The upper layer, a viscous oil, contains the benzenestearosulphonic acid with the remaining impurities insoluble in dilute sulphuric acid. If any stearosulphuric acid was present, this will have been decomposed by the heating into sulphuric acid and oxystearic acid and anhydrides. The lower layer is removed and the upper is washed with water containing hydrochloric acid until free from sulphuric acid. By this operation the benzenesulphonic acid is also washed out. The oily layer is now washed a number of times with petroleum ether, which dissolves the oleic acid, the benzene, and the other fatty matters before mentioned, leaving the compound pure except for small quantities of water and hydrochloric acid, and these can easily be removed by drying at 100° C.

The washing with petroleum ether is a tedious process, as some of the decomposition products of oleic acid are rather difficultly soluble in this liquid. For this reason, when quantitative results are not required, it is better to dissolve the partially purified product in ether and shake with water. The aqueous extract, containing most of the benzenestearosulphonic acid, is treated with a little hydrochloric acid, taken up with ether and again extracted with water. On evaporating the aqueous solution the compound is obtained in a pure state.

The composition of the compound was determined by the estimation of the sulphur and carbon and by its acid equivalent, it being a dibasic acid containing an acid hydrogen of the sulphonic radical, which can be exactly titrated by using methyl orange as indicator, and an acid hydrogen of the fatty radical which can be titrated with phenolphthalein as indicator.

The several analyses represent samples prepared at different times.

	Sulphur.	Carbon.	Ratio of sulphur to carbon.	$n/10$ alkali required to combine with SO_3H group in 1 gram of substance. Methyl orange as indicator. cc.	Additional $n/10$ alkali required to combine with the fatty group. Phenolphthalein as indicator. cc.
Calculated for $C_{10}H_6.SO_3H.C_{18}H_{35}O_2$.	7.2727	65.45	9.00	22.727	22.727
Found 1				21.56	22.41
" 2	7.12			22.49	22.44
" 3	7.22	64.70	8.96	22.66	23.19

The composition was further fixed by the determination of the weight of benzenestearosulphonic acid obtained from the oleic acid which entered into the reaction. From the molecular weights of the two compounds, 282 parts of oleic acid would yield 440 parts of benzenestearosulphonic acid, or the yield on 100 parts of oleic acid would be 156.03.

An accurately weighed, quantity of oleic acid was mixed with benzene and then treated with an excess of sulphuric acid. After removing the impurities soluble in acidified water, the product was extracted with petroleum ether, the extract weighed and deducted from the amount of oleic acid taken. The difference was that which had combined with benzene and sulphuric acid. The residue insoluble in petroleum ether was also dried and weighed, giving the yield of benzenestearosulphonic acid.

In two experiments 100 parts of oleic acid were found to yield 151.0 and 156.7 parts of benzenestearosulphonic acid.

In this calculation there is an error, in that the petroleum extract does not consist wholly of unaltered oleic acid, but also contains oxystearic acid and anhydrides; but this error is very small considering the small quantity of oleic acid deducted as a correction, and the fact, established by an experiment, that the weight of the fatty matter is only slightly altered on treating oleic acid alone with sulphuric acid and then decomposing by boiling with water.

Benzenestearosulphonic acid resembles in its physical characteristics, and also in many of its chemical ones, the stearosulphuric acid obtained by acting on oleic acid in the cold with concentrated sulphuric acid. At 100° C. the dry compound is a very viscous oil, while at ordinary temperatures it is a sticky, semisolid mass. It, as well as its mono- and di-alkaline salts,

is soluble in water in all proportions, yielding colloidal solutions which, on agitating, form a strong lather and are precipitated (salted out) by any strong acid, base or salt. The free acid is perfectly stable in boiling water, even in the presence of mineral acids, differing in this from stearosulphuric acid. On heating to high temperatures with hydrochloric acid it decomposes only very slowly. A small quantity heated in a sealed tube to 170° C. for three and a half hours, had decomposed only to the extent of 15 per cent.

Benzenestearosulphonic acid when fused with caustic potash gives potassium sulphite. Here again it differs from stearosulphuric acid, which when similarly treated yields potassium sulphate.

As shown by the formula, benzenestearosulphonic acid is dibasic, the two acid hydrogens having very different strengths, so that, as has been already pointed out, they can be independently titrated with caustic soda solution, using different indicators.

NAPHTHALENESTEAROSULPHONIC ACID,

$$C_{10}H_6(SO_3H)C_{18}H_{35}O_2.$$

This compound is prepared and purified in a manner precisely similar to that used in the preparation of the benzene compound, which it closely resembles, being, however, rather less fluid in its character.

The analysis gives the following results:

		n/10 alkali required to combine with the SO_3H group in one gram of substance. Methyl orange as indicator. cc.	Additional *n*/10 alkali required to combine with the fatty group in 1 gram of substance. Phenolphthalein as indicator. cc.
Calculated for $C_{10}H_6.SO_3H.C_{18}H_{35}O_2$		20.408	20.408
Found	1	20.07	19.97
"	2	20.28	20.17
"	3	20.35	20.41

PHENOLSTEAROSULPHONIC ACID,

$$C_6H_3OH(SO_3H)C_{18}H_{35}O_2.$$

This compound is prepared like the others and closely

resembles them in its character. The following analytical results show that the compound had not been obtained pure.

	n/10 alkali required to combine with the SO_3H group in 1 gram of substance. Methyl orange as indicator.	Additional *n*/10 alkali required to combine with the fatty group in 1 gram of substance. Phenolphthalein as indicator.
	cc.	cc.
Calculated for $C_6H_3OH.SO_3H.C_{18}H_{35}O_2$.	21.929	21.929
Found 1	24.47	20.39
" 2	29.75	20.77

These results clearly indicate the presence of a disulphonic acid. This I have not yet attempted to separate, but its quantity can be calculated and allowed for, and if this is done it will be seen that the figures will agree closely with those required by the formula.

In much of the analytical work described in this paper and also in the preparation of some of the compounds, I was kindly assisted by Mr. Wm. Simonson.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 12.]

A NEW INTERRUPTER FOR THE KOHLRAUSCH-OSTWALD CONDUCTIVITY METHOD.

BY J. LIVINGSTON R. MORGAN.

Received December 7, 1899.

IN a recent paper[1] I described three useful additions to the Kohlrausch-Ostwald conductivity method. Since then an improvement has been made in the interrupter, the first of the three described, which simplifies it to such an extent that a description of it is deemed advisable. In the apparatus as first proposed, the primary current (2–5 volts from the electric light circuit or from storage cells) was used to charge the vibrating wire as well as to excite the electromagnet. The current from the cell used in the conductivity apparatus was then connected, through the vibrating wire and an extra mercury cup, to a small induction coil (without the breaker), the secondary of the coil being connected to the bridge arrangement in the usual way. The intermittent current produced by the vibrating wire and the mercury cup becomes a rapidly alternating one, such as is desired, in passing through the induction coil.

[1] This Journal, **22**, 1 (1900).

In the new form, one of the mercury cups is dispensed with entirely, and the current from the cell of the conductivity apparatus alone goes through the wire causing it to vibrate, and thus with the mercury cup to make and break the circuit. In the Pupin arrangement[1] using the permanent magnet, one cell is

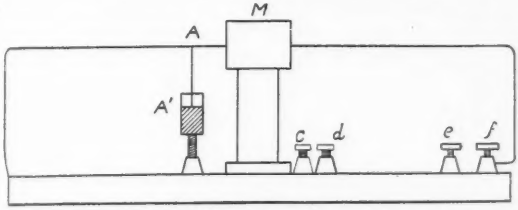


Fig. 1.—*c* and *d*, the binding posts of the electromagnet, are connected to the electric light circuit (3 to 5 volts). *c* is connected under the base to the mercury cup *A'*.

insufficient to cause a vibration but by the use of an electromagnet the strength of the magnetic field can be so intensified that the wire is repelled even when carrying a very small current. Fig. 1 shows the arrangement of the new form of

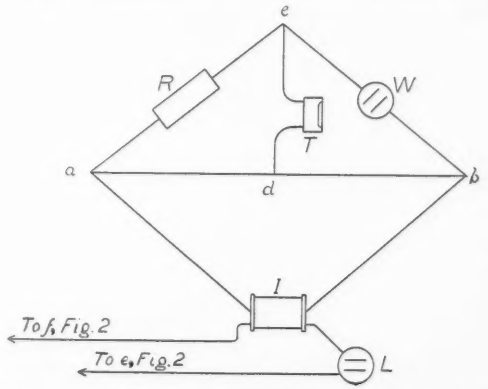


Fig. 2.—R is the known resistance, W the electrolytic cell, I the coil, L the Lelanché cell and T the telephone. The current breaker of the coil I is removed.

apparatus. The electromagnet is excited by a current of from 2 to 5 volts entering at the posts *c* and *d*. The current from the battery *L* (Fig. 2) is connected to the primary of the induction coil *I* through the posts *e* and *f* (Fig. 1). The dipper of the

[1] *Am. J. Sci.* [3], **45**, 325 (1893).

wire A is in contact with mercury A' in the adjustable cup, which is connected by a wire under the base to the post e. The current then goes from one pole of the battery L to f, A, A', e and then through the primary of the induction coil back to the other pole. When the current is passing through the wire the magnet will repel the wire, and if the cup A' is at the proper height the contact with the mercury will be broken and since the wire when uncharged is not affected by the magnet its tension will make the contact once again and the same process will be repeated. The tension of the wire and consequently the rapidity of vibration, may be altered by the screw devices at each end.

This new form of apparatus is not only simpler in construction than the original, but is also much more readily adjusted and kept in adjustment. In the earlier form with two mercury cups it is necessary that the wire vibrate in such a way that loops are formed at the two cups, so that the original adjustment is more difficult to make and a variation in the number of vibrations per second is less easy to arrange. If three or more pieces of conductivity apparatus, each with its cell, are connected to the same vibrator, a smaller voltage may be used for the electromagnet, for the voltage in the wire is much greater and consequently the strength of the magnetic field may be much reduced and still give the same result.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 13.]

THE SPECIFIC GRAVITY AND ELECTRICAL RESISTANCE OF METALLIC TELLURIUM.

BY VICTOR LENHER AND J. LIVINGSTON R. MORGAN.

Received January 2, 1900.

IN this Journal[1] one of us described the preparation of metallic tellurium by means of the reduction of an alkaline solution of the oxide of tellurium with sugar. A description was given in that paper of the means used to test the tellurium for impurities. The tellurium obtained by reducing with sugar was found to be volatile in hydrogen gas leaving no residue. Its oxide was found to be completely volatile in hydrochloric acid gas.

[1] Lenher: This Journal, 21, 348.

As a further means of establishing the purity of the metal, a few physical tests were made. The specific gravity was carefully determined and a great deal of time was spent in attempting to determine its electrical resistance.

Determination of the Specific Gravity.—For this purpose, material was selected, which had been twice distilled in hydrogen.

The metal was finely powdered, as a number of preliminary experiments showed that owing to the great crystalline tendency that the metal exhibits, it is almost impossible to obtain a specimen of any size which does not contain gas. Consequently, it was found that reasonably constant results could be obtained only when the metal was carefully broken up.

The experiments were carried out in an ordinary 15 cc. pycnometer, pure water being used as the medium. The temperature was 20°. In order to expel the adhering air bubbles, the water with the metal was heated and the vessel allowed to stand over night to cool.

	Weight tellurium taken.	Sp. gr.
Experiment 1....	11.9727	6.194
" 2	11.9146	6.200
" 3	16.0946	6.204
Mean		6.1993

This figure is a trifle less than that obtained by Spring[1] but is almost identical with that obtained by Klein and Morel[2]. The latter chemists obtained the figures 6.204 and 6.215, while Spring obtained a figure slightly higher, 6.22.

The latest figure previous to our work is by Priwoznik[3] who obtained 6.2459 at 18.2°.

Determination of the Electrical Resistance.—For the determination of the electrical resistance of a metal, it is advisable to obtain great length and small diameter of the substance. With tellurium this is almost impossible. The metal is extremely crystalline, more strongly so than any metal which has come into our hands. As a result of this tendency, the metal, when of small diameter and possessing any appreciable length, is so weak that a rod grasped by the end will snap off, it not being able to sustain its own weight.

[1] *Bull. Acad. Roy. Belg.* [3], **2**, 88-110 (1881).
[2] *Ann. Chem.* (Liebig), [6], **5**, 61
[3] *Chem. Centrbl.*, **2**, 962 (1892).

It is not practical to cast the metal in cold moulds. Various attempts were tried in this direction but proved unsuccessful. The best method for obtaining a suitable section was found to be to melt the metal in a thin glass tube of comparatively narrow bore. To this end an open glass tube was placed in an inclined combustion furnace and inside of it was introduced a smaller tube closed at one end and containing the metal to be fused. The fusion took place at a low red heat, while in the liquid condition, the tube was gently tapped until all of the gas escaped.

Slow cooling tends to produce larger crystals and the metal is correspondingly more brittle. Rapid cooling, on the other hand, gives smaller crystals, but the difference in resistance is not apparent. The most satisfactory results were obtained by jacketing the tube of molten tellurium with a larger tube also containing fused metal. Although in this instance the metal cooled under the pressure of the shell in the jacket, the only apparent difference was that longer sticks could be obtained.

From the many fusions that have been made in this laboratory, it appears that tellurium on cooling, first contracts until it solidifies, then slightly expands. As an example of this may be noted that each stick contained a depression in its upper part, which extended about one-fifth of the entire length[1] and that the tubes always cracked just after the metal solidified. The tubes invariably cracked at this time, no matter how carefully they had been annealed, nor how slowly they were cooled.

In order to obtain the best possible contact, a piece of rubber tubing was drawn over each end of the stick to be measured and the tubes filled with mercury. The latter was connected with a small dry battery, a wheatstone bridge and galvanometer being in the circuit.

No. 1.—Length, 100 mm., diameter, 7.42 mm. Resistance at 20° = 1.38 legal ohms. Specific resistance = 596.6.

No. 2.—Length 162 mm., diameter, 8.89 mm. Resistance at 20° = 1.23 legal ohms. Specific resistance = 463.6.

No. 3.—Length, 137 mm., diameter, 8.255 mm. Resistance at 20° = 1.46 legal ohms. Specific resistance = 569.9.

No. 4.—Length, 103 mm., diameter, 3.43 mm. Resistance at 20° = 3.68 legal ohms. Specific resistance = 330.1.

[1] This portion was always removed before measurements were made.

No. 5.—Length, 82 mm., diameter, 3.43 mm. Resistance at 20° = 2.48 legal ohms. Specific resistance = 279.4.

This specimen was a piece of No. 4 after a portion had been broken off.

No. 6.—Length, 84.5 mm., diameter, 3.05 mm. Resistance at 20° = 5.88 legal ohms. Specific resistance = 508.3.

No. 7.—Length, 86.1 mm., diameter, 4.83 mm. Resistance at 20° = 5.37 legal ohms. Specific resistance = 1152.

On close examination this bar was found to be cracked.

No. 8.—Length, 57.5 mm., diameter, 2.92. Resistance at 20° = 4.68 legal ohms. Specific resistance = 544.5.

As all of the bars showed a strong cleavage on the ends, the measurements could only be approximate, and when they are calculated to the standard conditions, one meter in length, with a cross section of one mm., the errors of measurement are correspondingly multiplied.

By using an ordinary copper clamp contact, almost any resistance can be obtained according to the amount of pressure exerted by the clamp; no difference in resistance could be detected when working in the light or dark.

By comparison of the results obtained, it will be observed that the mean would be about 500; however, from the great tendency to crystallization that the metal shows, it would seem more probable that the lowest result more nearly approaches the true figure. As gas carbon has a specific resistance equal to 50, the resistance of tellurium is seen to be enormous. The result obtained by Matthieson,[1] 0.000777 for the conductivity compared with silver as 100, would give a specific resistance of more than 2000, showing that the structure of his metal must have been different from ours or that different contact was made.

THE VOLUMETRIC DETERMINATION OF MAGNESIA.

By James Otis Handy.

Received January 2, 1900.

EVERY chemist, who has to make many determinations of magnesia in water, cement or other material, appreciates the difficulties surrounding the gravimetric process. These difficulties chiefly arise from the fact that the change from magne-

1 *Pogg. Ann.*, 103, 428.

sium ammonium phosphate to the pyrophosphate of magnesia is attended by a rapid consolidation or sintering of the mass. By this means particles of carbon from the filter-paper are often firmly enclosed in the lumps of precipitate.

If gradual heating over a Bunsen burner is continued long enough, fifteen minutes over the blast-lamp with crucible inclined and cover placed in a position to facilitate oxidation, will give a pure white pyrophosphate. If, however, the preliminary heating proceeds too rapidly, or is not continued long enough before applying the blast, it is almost impossible to burn off all the carbon.

The method recommended by Fresenius for completing the oxidation of such material by treatment with nitric acid followed by evaporation and re-ignition, yields a pure white residue, but the result is invariably low. The author found that pure magnesium pyrophosphate when so treated lost weight every time, although no mechanical loss took place. Moreover, repetition of the treatment caused further serious loss. Constant weight was not reached.

No one who has adopted the volumetric method for determining calcium oxalate by means of standard permanganate would ever go back to the gravimetric way. When a simple and accurate method for the volumetric determination of magnesia appears, it will be equally useful.

The alkalimetric method published by Stolba in 1866[1], referred to by Sutton, Hart, Meade[2] and others, has not come into general use. The reaction is:

$$MgNH_4PO_4 + H_2SO_4 = MgSO_4 + NH_4H_2PO_4.$$

Its unpopularity is doubtless due to the use of alcohol for removing the ammonia wash from the magnesium ammonium phosphate precipitate, it being an expensive and tedious procedure.

Meade proposes a radical change from the usual phosphate method. He estimates the magnesia by precipitating it as arsenate and determines by standard thiosulphate the amount of iodine which a hydrochloric acid solution of the precipitated arsenate liberates from potassium iodide. The procedure seems

1 *Chem. Centrbl.*, 728 (1866).

2 This Journal, **21**, 746 (1899).

rapid and accurate, but it would appeal only to those who prefer an iodometric to an alkalimetric method.

The writer has endeavored to eliminate the objectionable feature of Stolba's method by discarding alcohol and removing the free ammonia from the phosphate precipitate by taking advantage of the volatility of ammonia.

It was necessary to find some way of expelling the ammonia without in any way affecting the integrity of the phosphate which should remain. In view of the fact that Fresenius, Roscoe and Schorlemmer, and other authorities all agree that the only change which $MgNH_4PO_4.6H_2O$ suffers at 100° C., is the loss of 5 molecules of water of crystallization, it seemed a simple thing to put filter and precipitate into 50 cc. of distilled water, and after removing the ammonia by boiling down to 30 cc., to cool, add a measured excess of standard acid to dissolve the precipitate, and then to titrate back with standard alkali. After many trials in which the results were all low and irregular this method was abandoned. Evidently some change of composition took place at 100° C. under these conditions.

Other means of subjecting the ammoniacal precipitate to this temperature were tried. The filters containing the precipitates were spread out flat on strong 5-inch filters, and were placed, one set at a time, in a funnel through which a current of steam was rising, and allowed to remain for ten minutes. The ammonia was expelled, but the results by titration were still low, although absolutely no mechanical loss or loss by solution took place. There was a loss in alkalinity due to a chemical change other than the loss of water of crystallization.

Thinking that the presence of water in the one, and of steam in the other of these experiments, might have brought about a change which temperature alone could not have accomplished, a set of experiments were made wherein the filters and precipitates were dried in an oven at 100° C., away from all but the moisture which they at first contained. By this means also, low results were obtained.

It was then apparent that no rapid or satisfactory method could be based on titration of magnesium ammonium phosphate which had been dried at 100° C., or even heated to that temperature without drying. Although the change in alkalinity

might be perfectly definite and complete, it would require much longer for large precipitates to be completely transformed than for small ones, and irregular results would surely be obtained.

Before rejecting the statement of such eminent authorities with regard to the effect of drying magnesium ammonium phosphate at 100° C., it was thought best to completely eliminate the moisture element from the experiment.

A quantity of the pure salt was prepared by precipitation under standard conditions from a solution of magnesium chloride. After washing thoroughly with 10 per cent. ammonia wash (1 part of ammonium hydroxide, sp. gr. 0.90, mixed with 9 parts of water), the precipitate was spread out on filter-paper and allowed to dry in the air. It was then dried over sulphuric acid, after which it was ground, mixed and placed in a stoppered bottle. Weighed portions were then tested for purity, and this having been established, the property in question was examined into.

PROPERTIES OF $MgNH_4PO_4.6H_2O$.

	Statement of authorities. Per cent.	Actual facts. Per cent.
Loss of weight at 100° C. (water, etc.)	36.70	41.43
Yield of $Mg_2P_2O_7$ on ignition.....	45.34	45.59
Cc. $\frac{N}{10}$ H_2SO_4 for 1 gram before 100° drying	82.05	81.94
The same if dried at 100° C. beforehand.....	82.05	54.59
Loss of original alkalinity at 100° C. (per cent.)	00.00	33.38

The author does not wish to be understood as saying that the first column in the above table represents verbatim the statements of Fresenius and others, but that it does represent the exact results which would follow if their statements were true.

By comparing the magnesium oxide value of decinormal sulphuric acid when used on air-dried $MgNH_4PO_4.6H_2O$ with the value when a weighed amount of the same salt is heated to constant weight at 100° C. before titration, it will be seen that the difference is very great.

1 cc. $\frac{N}{10}$ H_2SO_4 = 0.002 gram MgO in the air-dried salt.

1 cc. $\frac{N}{10}$ H_2SO_4 = 0.003 gram MgO in the same material if first dried at 100° C.

Although the definiteness of this change is now firmly established, the formula of the compound which is formed at 100° C., has not yet been determined.

The folly of drying at 100° C. as a preliminary to the titration of $MgNH_4PO_4.6H_2O$ having been established, the author determined to ascertain the speed with which ammonia evaporated from phosphate precipitates at ordinary temperature. It was found that if filters containing precipitates were opened flat after washing, and placed face upward on heavy dry filter-paper of the sort made by Whitall, Tatum & Co., for druggist's use, the bulk of the moisture would be drawn out in a few minutes, and if transferred then to a second dry paper and allowed to stand for half an hour to one hour, the ammonia, so far as its power of neutralizing a measurable quantity of acid was concerned, had entirely disappeared. When the filter-papers have become dry for a distance equal to one-fifth of the diameter of the paper, measured from the outer rim, it is certain that the ammonia has been expelled. This is, of course, based on the assumption that the precipitate is distributed fairly evenly over the rest of the paper.

Methyl orange was the indicator used, and in all cases a clear yellow was considered the end-point when using decinormal sodium hydroxide to measure the excess of decinormal sulphuric acid.

TITRATION OF $MgNH_4PO_4.6H_2O$.

	Time for precipitation. Hrs.	Min.	Time of drying. Hrs.	Min.	Temperature.	MgO used. Gram.	MgO found. Gram.	Error. Gram.
1	3	0	18	6	21° C	0.00475	0.00478	0.00003
2	3	0	18	6		0.01900	0.01900	0.00000
3	3	0	18	6		0.02375	0.02377	0.00002
4	3	0	18	6		0.04750	0.04785	0.00035
5	1	30	2	0	19	0.02375	0.02377	0.00002
6	1	30	2	30	19	0.02375	0.02377	0.00002
7	1	30	3	0	19	0.02375	0.02377	0.00002
8	1	30	3	20	19	0.02375	0.02377	0.00002
9	1	30	2	0	19	0.02375	0.02377	0.00002
10	1	30	1	0	19	0.02375	0.02377	0.00002
11	1	30	1	0	21	0.04750	0.04775	0.00025
12	1	30	1	30	21	0.01907	0.01990	0.00083
13	1	30	1	30	21	0.01907	0.01930	0.00023
14	1	30			21	0.03814	0.03830	0.00016
15	1	30	1	30	21	0.05720	0.05740	0.00020
16	1	30	1		21	0.05720	0.05780	0.00060
17	1	30		30	21	0.01907	0.01920	0.00013
18	1	30		30	21	0.01907	0.01920	0.00013

	Time for precipitation. Hrs.	Min.	Time of drying. Hrs.	Min.	Temperature.	MgO used. Gram.	MgO found. Gram.	Error. Gram.
19	1	30	0	45	21	0.03814	0.03830	0.00016
20	1	30	1	15	21	0.03814	0.03800	0.00014
21	1	30	1	0	21	0.05720	0.05670	0.00050
22	1	30	1	0	21	0.05720	0.05680	0.00040
23	1	30	0	25	65	unknown	0.05650	
24	1	30	0	25	65	unknown	0.05650	
25	1	30	1	15	21	unknown	0.05650	
26	1	0	1	0	21	0.04767	0.04711	0.00056
27	1	0	0	20	59	0.04767	0.04771	0.00004
28	1	0	0	40	62 av. 66 max.	0.04767	0.04671	0.00096
29	1	0	1	0	62 av. 66 max.	0.04767	0.04631	0.00136
30	5 shaking 30 standing				60	21	0.00095	0.00090	0.00005
31	5 shaking 45 standing				60	21	0.00048	0.00050	0.00002

Experiments like the above prove the accuracy of the alkalimetric method for magnesia determination. The cases of significant error in the table may be divided into those caused by imperfect removal of the ammonia (Nos. 12 and 16); those caused by drying too long and at too high a temperature in the oven (Nos. 28 and 29); those doubtless caused by imperfect manipulation (Nos. 21, 22, and 26); and, finally, those inherent in the process itself. The latter are all very small if, indeed, they exist at all. Experiments 23, 24, and 25 are comparative only.

Experiments Nos. 30 and 31 show not only the extreme delicacy of the reaction on which the method depends, but they show how rapid the reaction is, even in very dilute solutions, and how insoluble the phosphate is in 10 per cent. ammonia wash.

It was found that five minutes' shaking in a stoppered flask at ordinary temperature sufficed, if followed by fifteen minutes' standing, to completely precipitate any magnesia solution containing as much as 0.002 gram of magnesium oxide in 100 cc. With amounts exceeding 0.05 gram per 100 cc., it is believed that filtration could be begun in five minutes after the end of the shaking process.

In order to ascertain what temperature could be safely used to expedite the expulsion of ammonia from the phosphate precipitates, a series of experiments were made. It was found that

at 55° C. there was no appreciable loss of alkalinity but that at 65° a loss of 1 per cent. had taken place. Several experiments in which the filters and precipitates were removed from the oven as soon as the outer half-inch of the papers were dry, gave identical results with air-drying at 21° C. From fifteen to thirty minutes in the oven at 50° to 60° C. suffices. If the drying of the precipitate proceeds too far, solution in decinormal sulphuric acid is slow. If, however, the drying is stopped at the point described there is enough moisture left so that, on stirring, the precipitate blends quickly with the acid and soon dissolves.

For the drying a large, rectangular, double-walled oven of the kind sold with oil or gas stoves is cheap and convenient.

Unless magnesia determinations are constantly being made, it will often be more convenient to let the precipitates air-dry than to use an oven.

The tendency of magnesia to precipitate with iron and alumina and with calcium oxalate must be met by re-solution in hydrochloric acid and reprecipitation. When the amount of lime is considerable, it is best to burn off the first oxalate precipitate before dissolving in hydrochloric acid. By this means the oxalate is decomposed and the addition of ammonia alone does not cause its sudden reprecipitation. Even in the second precipitation, if the boiling is allowed to proceed longer than is necessary to make the finely crystalline calcium oxalate settle well, some magnesium oxalate is sure to precipitate, betraying its presence by its coarser texture. The solution for magnesia precipitation usually does and always should contain in the form of ammonium chloride the equivalent of 5 cc. of concentrated hydrochloric acid per 100 cc.

THE METHOD.

Add ammonia (sp. gr. 0.90), equivalent to one-tenth of the solution. Cool in water to 20° to 25° C. Precipitate by adding slowly with constant stirring a saturated solution of sodium ammonium phosphate, using 1 cc. for each 0.01 gram magnesium oxide. Stir vigorously for about five minutes or shake in a flask for an equal length of time. In the former case let the solution stand until the clarification of the upper liquid shows that the reaction is complete. In the case of flask precipitations,

if over 0.002 gram of magnesium oxide is present the solution may be filtered in fifteen minutes. Suction may be used if desired but if many solutions are to be filtered at once little is gained by its use. Use 10 per cent. ammonia wash (one part ammonia (sp. gr. 0.90) to nine of water). Deliver it preferably from an aspirator bottle placed about 4 feet above the bench. Wash by decantation as far as possible. Finally wash the precipitate which has gone on the filter, back into the beaker, stir it up with the ammonia wash and bring it again completely on the filter-paper. Wash once more, leaving the upper edge of the filter clear of precipitate so that it can be handled. Avoid assembling all of the precipitate in the apex but leave it fairly evenly distributed over the lower two-thirds of the paper. Allow the precipitates to drain and then transfer each in turn to a dry 5-inch filter-paper, allowing them to remain there open and face upward until the bulk of the moisture has been absorbed. After about three minutes transfer them to fresh dry filters, and in the case of heavy precipitates to a third set a few minutes later. Then place the filters on a shelf to dry at the temperature of the room or place filter-papers and backing on the grating of an air oven having a temperature of 50° to 60° C. After fifteen or twenty minutes in the oven or forty-five minutes in the air, watch for the time when the filters have dried inward half an inch from the margin. This appearance has been found to indicate that the evaporation has gone far enough to insure the expulsion of the free ammonia. The precipitates and filters may then be removed and placed in small dry beakers where they are treated each with a measured excess of decinormal sulphuric acid, and stirred until the papers are disintegrated and the precipitates dissolved. Two drops of a 0.1 per cent. alcoholic solution of methyl orange are then added. If this gives a clear decided pink, enough acid has been added. If it is only faintly pink the excess of acid is slight and some minute particles may have escaped solution. In such cases add five cc. more decinormal sulphuric acid and stir well. Finally dilute to about 100 cc. and titrate back with decinormal sodium hydroxide solution to the appearance of a clear yellow color, free from all suggestion of pink.

1 cc. $\frac{N}{10}$ H_2SO_4 = 0.002 gram MgO.

If filtrations have taken place during the latter part of the day the filters may be removed from the funnels and allowed to stand over night after which they are titrated as described.

The writer hopes that the simplicity and accuracy of the method may render it generally useful.

PITTSBURG, December 25, 1899.

A PRELIMINARY COMMUNICATION UPON RICININE.

BY THOMAS EVANS.

Received January 2, 1900.

TUSON[1] obtained a substance crystallizing in plates which he called ricinine, by extracting castor beans, the seed of the *Ricinus communis*, with boiling water, filtering, evaporating to a thick sirup and again extracting with boiling alcohol.

Tuson states that ricinine is soluble in water and alcohol and very little soluble in ether and benzene, and that when heated with solid potassium hydroxide ricinine evolves ammonia.

He describes, but gives no analyses of crystalline compounds obtained by the action of nitric acid, mercuric chloride, and platinic chloride.

No salts with acids, with the possible exception of the nitric acid salt, were obtained by Tuson.

A few years later Werner[2] claimed that the ricinine of Tuson contained no nitrogen and was the magnesium salt of an acid with the formula $C_{11}H_{20}O_{10}Mg_2.2H_2O$. To this Tuson[3] replied that Werner had evidently investigated an entirely different substance, as his ricinine contained 20.79 per cent. of nitrogen.

Schulze[4] obtained a nitrogenous substance from the germinated seed of *Ricinus communis*, by extracting with alcohol, distilling this off, taking up the residue with water, treating with tannic acid and lead acetate, filtering, removing lead with hydrogen sulphide, and evaporating the filtrate to small bulk.

The impure product was purified by boiling the aqueous solution with animal charcoal and finally by crystallizing from absolute alcohol, from which it separated in small colorless prisms melting at 193° C.

1 *J. Chem. Soc.*, 17, 195.
2 *Jsb. d. Chem.*, 877 (1870).
3 *Ibid.*, 877 (1870).
4 *Ber. d. chem. Ges.*, 30, 2197.

Schulze says he is unable to identify this body with any known substance and calls it ricidine, assigning it the formula $C_{12}H_{13}N_3O_3$.

Pictet[1] gives ricinine the formula $C_{17}H_{18}N_4O_4$ but makes no reference to the original article from which this formula was obtained.

In the following investigation finely ground castor press cake, known as castor pomace, which was kindly furnished by The Brown Oil Co., of St. Louis, was used as a raw material. This was extracted by both Tuson's and Schulze's methods and in each case the same product was obtained, thus identifying the ricidine of Schulze with the ricinine of Tuson.

Tuson's method of extraction was found to be less satisfactory than that of Schulze, although the product so obtained was much lighter in color. It was found advantageous to modify Tuson's process, and use boiling toluene instead of alcohol to extract the residue from the evaporation of the aqueous extract. Upon sudden cooling of the toluene solution ricinine deposits on the sides and bottom of the containing vessel, in small, almost colorless prismatic crystals, which are frequently crossed and sometimes whetstone shaped, and which adhere tightly to the walls of the vessel.

The ricinine so obtained was purified by recrystallization from alcohol, from which it deposited in small plates frequently united to form rosettes. The melting-point was 193° C. and the analysis gave the following results, which agree very well with Schulze's figures:

	Calculated for $C_{12}H_{13}N_3O_3$.	Calculated for $C_{16}H_{16}N_4O_4$.	Calculated for $C_{16}H_{18}N_4O_4$.	Schulze.		Evans.
Carbon	58.30	58.54	58.18	58.20	58.44	58.20
Hydrogen	5.26	4.88	5.45	5.15	5.31	5.06
Nitrogen	17.00	17.07	16.97	17.11	17.15	

In order to render the extraction by Schulze's method more complete a brass extractor of the Soxhlet type was constructed; this held about 900 grams of pomace and was surrounded by a brass jacket, forming an air space between the two, through which the alcohol vapor could ascend to the return condenser, thus keeping the alcohol hot in the extractor. Later on it was found advantageous to place an additional jacket of asbestos around the brass one.

[1] Les Alcaloides vegetaux, 2nd. ed.

The dark brown alcoholic extract was treated according to Schulze's directions, giving a dark brown aqueous solution of ricinine from which yellowish brown crystals deposited on standing for twelve hours or longer.

Further evaporation of the mother-liquor gave a small amount of the substance; it was found impracticable to further concentrate the second mother-liquor, but upon diluting it with water, precipitating with subacetate of lead, filtering, precipitating out the excess of lead with hydrogen sulphide, filtering and evaporating to small bulk, more crystals of ricinine were obtained. An attempt to remove the brown color of the solution with animal charcoal, either before or after treatment with subacetate of lead, proved unsuccessful.

The impure product was purified by boiling its aqueous solution with animal charcoal. So prepared the substance showed a melting-point of 193° uncorr., and was evidently the same as the product obtained by the aqueous extraction of the pomace, as both gave the reddish purple color obtained by Schulze[1] by dissolving a few crystals in concentrated nitric acid, evaporating to dryness on the water-bath, taking up with water and again evaporating, and finally adding a drop of ammonia water.

To make sure that the product obtained by the extracting of the castor pomace was the same as Tuson obtained by the extraction of the beans, a quantity of these were extracted by his process and yielded a crystalline substance melting at 193° and was evidently the same as the products already described.

While it was found that neither sample of ricinine gave precipitates with silver nitrate, mercuric nitrate, or mercuric chloride, both gave a feathery crystalline product on long standing of a mixture of cold concentrated solutions of ricinine and mercuric chloride.

The chlorplatinate described by Tuson seems to be due to the presence of some more highly nitrogenous body; this seems the more probable when we compare Tuson's percentage of nitrogen (20.79 per cent.) with that found by Schulze (17.11 per cent.).

The writer has obtained the chlorplatinate referred to, but in each case it was with a ricinine which was manifestly impure as

[1] *Ber. d. chem. Ges.*, 30, 2198.

it melted partially at 188° and was completely melted at 190°–191°.

Further investigations of the double salt with mercuric chloride, the products obtained by the action of nitric acid and ammonia, are now in progress.

BROMINE DERIVATIVE.

When bromine or bromine water is added to a moderately concentrated solution of ricinine in water, the resultant red solution decolorizes very slowly, and upon heating on the water-bath to drive out the excess of bromine, long colorless radial needles separate, either immediately after the expulsion of the bromine or, if the solution be more dilute, upon evaporation.

The product was purified by repeated crystallization from alcohol, 95 per cent., and upon heating in a capillary tube darkened at 220°–225° C. shrinking at the same time and melted at 229.5°–230° under decomposition and evolution of gas. By moderately rapid heating the melting-point was found at 232°.

Qualitative tests showed the substance to contain both bromine and nitrogen. Upon boiling the aqueous solution with 10 per cent. silver nitrate there was a very slight darkening of the solution but no precipitation of silver bromide, thus showing the substance to be a bromide and not a salt of hydrobromic acid.

The same bromide was obtained upon treating a chloroform solution of ricinine with bromine in chloroform, as follows:

Two grams of ricinine were dissolved in about 200 cc. of chloroform by boiling in a flask connected with a return condenser; to this solution 12 cc. of a solution of 10 cc. of bromine in 50 cc. chloroform was added. After about a minute a considerable precipitate formed and settled to the bottom of the flask. (Ricinine floats on chloroform and it seems probable that the precipitate consists of the hydrobromic acid salt of ricinine, along with some dibromricinine.)

After boiling for ten minutes copious fumes of hydrobromic acid were evolved from the top of the condenser; boiling was continued for some time after these fumes ceased to come off, in all about an hour. The precipitate formed at first did not appreciably increase or diminish during the boiling.

The flask and contents were allowed to stand over night, the precipitate filtered off, washed with chloroform, and the filtrate

evaporated to dryness on the water-bath, the heating being continued until the residue had lost nearly all of its yellow color. The weight of the residue, impure dibromricinine, equaled 2.06 grams, and the dried precipitate weighed 1.82 grams.

When the precipitate was dissolved in boiling alcohol and the solution allowed to cool, prismatic crystals were obtained melting at 192° uncorr., which were evidently unchanged ricinine, as they gave the characteristic reaction with nitric acid and ammonia, while the bromide gave no such reaction.

The weight of ricinine recovered was about 1 gram.

The residue from the evaporation of the chloroform filtrate gave beautiful, long, brittle needles, generally radiating in clusters from several points, and whose length was largely dependent upon the diameter of the beaker and the depth of the solution. These crystals gave the same melting-point, 230° C., as those obtained by brominating in aqueous solution, which would seem to indicate that ricinine was an acid amide or perhaps a diureide. It was at first thought that it might be a substituted uric acid, but the fact that the murexide test fails to give the characteristic color, when performed with potassium chlorate and hydrochloric acid, or with dilute nitric acid, makes this seem doubtful.

The analysis of the recrystallized bromide gave the following results:

Water of crystallization, none.

I. 0.3525 gram substance, dried at 120°, gave 0.5173 gram carbon dioxide, and 0.1084 gram water.

II. The substance was recrystallized from absolute alcohol and 0.2055 gram substance, dried at 120°, gave 0.3000 gram carbon dioxide, and 0.0561 gram water.

	Calculated for $C_{15}H_{14}Br_2N_4O_4$.	Calculated for $C_{16}H_{16}Br_2N_4O_4$.	I.	II.
Carbon	39.53	39.99	40.02	39.81
Hydrogen	2.88	3.27	3.41	3.03
Bromine	32.92	32.79	32.343	....
Nitrogen	11.52	11.42	12.28	11.97

The discrepancy between the results obtained and the theory is probably due to impurity in the form of ricinine. Lack of substance has prevented a more careful separation of the dibromide

from possible impurity; but with more substance more satisfactory results are expected.

The formula $C_{12}H_{12}N_2O_3$ proposed by Schulze does not suit the bromine derivative as well as the ones suggested above, as $C_{12}H_{19}BrN_2O_3$ calls for 24.54 per cent. of bromine and $C_{12}H_{11}Br_2N_2O_3$ for 39.50 per cent.

Ricinine dibromide is soluble in about 200 parts of 93 per cent. alcohol and in practically the same amount of water; it is rather less soluble in chloroform. From dilute solutions in alcohol or water it crystallizes in long needles, while from more concentrated solutions it is obtained as a mass of short, silky, white needles.

So far all attempts to make a bromide containing less bromine have proved unsuccessful, the same product being obtained with varying amounts of bromine.

Ricinine dibromide is soluble in hot, dilute, or concentrated hydrochloric acid and separates out unchanged on cooling. When treated with concentrated nitric acid and ammonia as described under ricinine, it gives no characteristic color.

Its aqueous solution appears to be neutral, and it was found impossible to prepare double salts with platinic or auric chloride.

OXIDATION OF RICININE.

Schulze states that upon oxidizing ricidine with potassium bichromate and sulphuric acid an odor of hydrocyanic acid was obtained, but does not mention other oxidation products.

Upon treatment of an alkaline solution of ricinine with potassium permanganate, the latter was almost immediately reduced, the reduction being accompanied with a faint odor of hydrocyanic acid. Upon filtering off the oxide of manganese a colorless solution was obtained, which became red with a yellow fluorescence upon acidifying with hydrochloric acid; when heated on the water-bath the solution became more intensely colored, and upon evaporation and subsequent cooling, beautiful, long, wavy, salmon-pink needles separated. These proved to be free from inorganic matter and were completely decolorized when their aqueous solution was boiled with animal charcoal.

The oxidation was carried out as follows:

One-half gram ricinine was dissolved in 20 cc. of boiling water

to which 5.5 cc. of approximately normal potassium hydroxide were added. After cooling to 17° C. a solution of potassium permanganate, containing 5.8 grams of the solid in 320 cc. of water, was slowly added until a further addition produced an evolution of a few bubbles of gas; in all 16 cc. of the permanganate were added.

The flask and contents were then allowed to stand for five hours; the oxide of manganese, which had settled, was filtered off after being washed by decantation. The filtrate and washings equaled 100 cc.

The colorless alkaline solution was heated on the water-bath, and made faintly acid with hydrochloric acid, when a few bubbles of carbon dioxide were evolved and the solution became red. Upon evaporation until crystals were deposited on the sides of the dish at the level of the liquid, and then allowing to stand, 0.27 gram of pink silky needles were obtained, melting, after previous blackening, at 269.5°. After repeated boiling of the aqueous solution with animal charcoal, the crystals were obtained snowy white; it was impossible to remove all of the color from the mother-liquor.

The purified substance melted at 279°—280°, becoming black several degrees below the melting-point.

The aqueous solution of the oxidation product is acid to litmus paper, and forms crystalline salts with alkalies as well as with silver nitrate. A test for the degree of acidity, using phenolphthalein as an indicator, gave the following results:

0.1079 gram acid dissolved in 50 cc. of water required 7.1 cc. standard alkali containing 0.001971 gram NaOH per cc., for neutralization; or 0.00805 gram Na, which equals 7.46 per cent. Na.

The acid contains nitrogen, and on evaporation with nitric acid and moistening with ammonia, gave the reddish purple color characteristic of ricinine, but to a lesser degree,—hence the thought that this may be due to impurity in the form of unoxidized ricinine.

A second portion of 1 gram of ricinine was oxidized in the manner already described, made acid with hydrochloric acid, and concentrated until 6 grams of reddish needles, mixed with dark red prisms, were obtained; these were filtered off and boiled with benzene for several hours, when a reddish yellow solution

with a green fluorescence was obtained, the prismatic crystals being dissolved while the needle-like crystals appear to be quite insoluble. Upon evaporation of the benzene solutions red prismatic crystals were obtained which became colorless with ammonia, and on evaporation of the solution so obtained gave a colorless crystalline mass.

The difficulty in preparing even small amounts of ricinine has materially interfered with the process of the investigation. The writer is now germinating seed in the dark, and hopes to be able to contribute further in the near future.

UNIVERSITY OF CINCINNATI,
December 29, 1899.

NOTES.

Retention of Moisture by Asbestos.—In the use of the Gooch crucible error may result from ignoring the fact that asbestos (some asbestos at any rate) retains moisture with great tenacity, so that after being dried at 100° C. to constant weight, the Gooch apparatus will suffer a further and notable loss of weight upon ignition over a Bunsen burner.

	Grams.
1. Dried one hour at 100° C., weighed	21.0452
Again dried one hour at 100° C., weighed	21.0450
Then ignited ten minutes, weighed	21.0441
2. Dried one hour at 100° C., weighed	21.0436
Then ignited five minutes, "	21.0429
3. Dried one hour at 100° C., "	21.0418
Again dried one hour at 100° C., weighed	21.0418
Then ignited five minutes, weighed	21.0409
4. Dried two hours at 100° C., "	20.7304
Then ignited one-fourth, weighed	20.7293
5. Dried three hours at 103° C., weighed	20.8250
Then ignited one-fourth hour, weighed	20.8246
6. Not dried in air-bath	.....
Ignited five minutes	21.0950
Then ignited again one hour	21.0944
7. Asbestos in larger quantity from a Hirsch funnel dried in a platinum crucible six hours at 90°–100° C.	20.2828
Then ignited one hour	20.2811
8. Ignited in a platinum boat in porcelain combustion tube in current of oxygen, then dried three hours at 100° C	21.1742
Then ignited one hour	21.1726

The asbestos used in these experiments was, of course, previously ignited and purified.

It is therefore necessary, when the weight of a dried precipitate is to be found, either to get the preliminary weight of the Gooch crucible by drying the same length of time, and at the same temperature as is intended with the precipitate; or much more conveniently, to find, once for all, the weight of the moisture retained by the dried Gooch crucible, and make the necessary correction when getting weights of precipitates.

GEORGE AUCHY.

The Determination of Graphite by Loss.—The figures given in the above note show that it is necessary to observe precaution in determining graphite in pig iron by the method of loss upon ignition, if the operator prefers the use of asbestos to that of a weighed paper disk or to counterpoised filters. Although the proposers of this method of determining graphite (Eggertz, Tamm, Crobaugh, Dougherty, Rodgars) are unanimous in directing the use of weighed paper for filtering, asbestos seems preferable for the reason that by its use the time and labor of drying and weighing the paper disk, or of drying and counterpoising the filters, is saved. With asbestos no weight is taken except that of the Gooch crucible plus graphite, etc., after drying, and again after ignition, the loss representing graphite. In the absence of a Gooch crucible the filtration may be made in a Hirsch funnel, or a Shimer funnel, and the asbestos and graphite then transferred to an ordinary crucible with the graphite part of the asbestos pressed against the wall of the crucible, as is also done when a Gooch crucible is used.

In using this method of loss upon ignition (filtering through counterpoised filters) Crobaugh obtained somewhat variable results (3.53 per cent. to 3.75 per cent.) which he attributed chiefly to non-homogeneity of the drillings. The presence of hydrated silica could not serve as an explanation, because the elimination of the silica by the addition of hydrofluoric acid during solution of the drillings, is a distinguishing feature of his method. The writer of this note also obtained varying results by the method, which, in his opinion were due, not to any lack of homogeneity in the drillings (mixed as they were by the aid of alcohol as recommended and found necessary by Shimer), nor

to the presence of gelatinous silica not completely dehydrated by the heat used in drying the graphite (Drown being strictly followed in dissolving the drillings as in phosphorus determinations), but probably to the fact that graphite thus obtained is not always pure carbon, but contains sometimes other combustible matter—combinations of hydrogen, oxygen, nitrogen, and sulphur in some form. For smaller percentages the method may serve. By combustion as usual, we obtain 3.21 per cent., 3.24 per cent; by loss upon ignition, 3.35 per cent., 3.36 per cent., 3.38 per cent., 3.20 per cent.

That gelatinous silica, if present, is not dehydrated by the drying of the graphite, was found by Tamm. An experiment by the writer showed 0.0094 gram water retained by about 0.13 gram gelatinous silica after being dried as graphite is dried.

GEORGE AUCHY.

The Persulphates of Rubidium, Cesium, and Thallium.—In the October part of this Journal,[1] there is a short paper by Foster and Smith on the above subject. As I have recently prepared and partially investigated these salts, I consider it advisable to publish the present note, retaining details for a paper to be published later.

The rubidium and cesium salts were prepared from ammonium persulphate by double decomposition, purified, and recrystallized. The crystals are not isomorphous with those of the potassium salt (triclinic), but with those of the ammonium salt (monoclinic). As mixtures of the potassium salt with the others have been obtained in well-formed monoclinic crystals, notwithstanding a great preponderance of potassium salt, it is evident that we have here to deal with an isodimorphous group.

The thallous salt has not yet been obtained pure, but mixtures of it with ammonium persulphate have been obtained in crystals isomorphous with the above monoclinic group. As the electrolysis of thallous sulphate solution would present interesting peculiarities, owing to the existence of thallic compounds, it was decided to investigate that subject also. It was found necessary to delay this, however, to permit of a preliminary investigation of thallic sulphate and its double salts, which is at present being carried out. Thallous persulphate, $Tl'_2S_2O_8$, is isomeric with thallous thallic sulphate, $Tl'Tl'''(SO_4)_2$ or $Tl_2SO_4Tl_2(SO_4)_3$.

UNIVERSITY OF EDINBURGH,
October, 1899.

HUGH MARSHALL.

[1] This Journal, **21**, 934 (1899).

OBITUARY.

Sir Edward Frankland.

WE are again called upon to note the departure of a co-worker and master in our chosen field of science. Eulogy is not necessary. The good he has achieved lives after him, and we would merely note that the researches of Sir Edward Frankland, extending over a period of thirty years, relate to work in pure, applied, and physical chemistry. Those in pure chemistry were conducted at first in the laboratories of Playfair, Bunsen, and Liebig. They include subjects related to each other as follows: the conversion of the cyanogen group into the carboxyl group; the change of the alkyl cyanides to the corresponding organic acids, the saponification of ethyl cyanide was announced by Edward Frankland and Hermann Kolbe when they were fellow assistants in Playfair's laboratory in 1845. Although this reaction was not then pursued beyond the monobasic acids, others applied it successfully in other directions. Then followed the action of metallic potassium upon ethyl cyanide and the polymerization of the latter, the isolation of the organic radicals, and the discovery of the organo-metallic compounds. Of these, which were investigated by Frankland throughout his scientific career, were zinc methyl and zinc ethyl, in the study of which the author remarks: "I had not proceeded far in the investigation of these compounds before the facts brought to light began to impress upon me the existence of a fixity in the maximum combining value or capacity of saturation in the metallic elements which had never before been suspected." The ready introduction of negative chlorine into bodies for a more electropositive constituent is a fact to which we give little thought. "The inverse process" in the day of Frankland "had been successfully accomplished in comparatively few cases." Through zinc methyl he succeeded in substituting methyl, ethyl, etc., for electronegative constituents, thus "opening up a most extensive and absolutely new field of research."

Next came the syntheses of acids of the lactic series, of the acrylic series (aiming here to produce the higher fat acids by direct synthesis from acetic acid), with the formation of ethers and ketones.

In applied chemistry Frankland studied the "hydrocarbon" process of gas-making and contributed much to the knowledge of gas manufacture. He also studied magnesium as a source of light.

In connection with his studies of the water supply of London he developed new and accurate methods for the determination of the amount of organic carbon and nitrogen in potable waters. As a member of the Royal Commission on the Pollution of Rivers he conducted, during a series of years, most exhaustive researches upon the question of water supply. Frankland also gave attention to the spectra of gases and inquired into the source of muscular power. He presented four or five papers relating to "climate," discussing the physical cause of the glacial epoch. Crooke's radiometer and colored solar halos also engaged his earnest thought.

The preceding lines indicate in a measure the scientific activity of the great investigator whose earthly career ceased on August 9, 1899, at the age of seventy-four years.

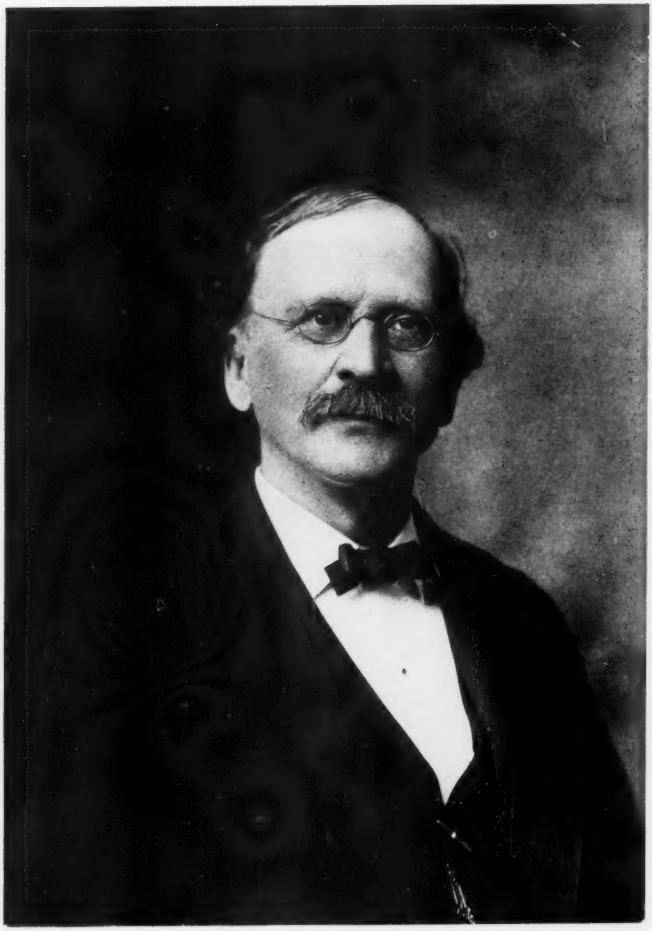
WM. A. NOYES,
A. B. PRESCOTT,
EDGAR F. SMITH,
Committee.

NEW BOOKS.

DETERMINATION OF RADICLES IN CARBON COMPOUNDS. By H. MEYER. Authorized translation by J. BISHOP TINGLE. New York: John Wiley and Sons. London: Chapman and Hall. ix + 133 pp. 12mo. Cloth. Price, $1.00.

This book is a translation of the original German edition with various corrections, additions, and changes in arrangement made partly by the author and partly by the translator. The successful methods known at present for the determination of organic radicals have been collected in the five chapters of this little volume, which deal with the following topics: Chapter I.—Determination of hydroxyl; Chapter II.—Determination of methoxyl, ethoxyl, and carboxyl; Chapter III.—Determination of carbonyl; Chapter IV.—Determination of the amino, nitrile, amide, imide, methyl imide, and ethyl imide groups; Chapter V.—Determination of the diazo group, the hydrazo radical, the nitro group, the iodoso group, the iodoxy group, the peroxide group, the iodine number.

The book contains then in compact form much valuable material that the student must ordinarily gather from various texts and periodicals. References to original articles are given. The improvements and additions have brought the book up to date. The translator has done his work in a commendable way. The excellent work of the publishers is too well-known to require further comment. LOUIS KAHLENBERG.



Edward W. Morley